# This Page Is Inserted by IFW Operations and is not a part of the Official Record

# BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

# IMAGES ARE BEST AVAILABLE COPY.

As rescanning documents will not correct images, please do not report the images to the Image Problem Mailbox.

# THIS PAGE BLANK (USPTO)

## **PCT**

# WORLD INTELLECTUAL PROPERTY ORGANIZATION International Bureau



#### INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

51) International Patent Classification 6:		(11) International Publication Number: WO 97/156
C09J 123/16	A1	(43) International Publication Date: 1 May 1997 (01.05.
21) International Application Number: PCT/EF 22) International Filing Date: 2 September 1996 (		DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC. NL,
30) Priority Data: 9521494.6 20 October 1995 (20.10.95)	) C	Published With international search report.
71) Applicant (for all designated States except US): CHEMICAL PATENTS INC. [US/US]; 1900 Ea Avenue, Linden, NY 07036 (US).	EXXC st Lind	on en
72) Inventors; and 75) Inventors/Applicants (for US only): FAISSAT, Micl [FR/BE]; Avenue Marie-Louise 21, B-1410 (BE). ROBBERECHTS, Herman, Diederik, Mar [BE/BE]; Ipsvoordestraat 43, B-1880 Nieuwenrod	Waterlinie, Em	oo   iel
74) Agents: BAWDEN, Peter, Charles et al.: Exxon Limited, Exxon Chemical Technology Centre, P.O. Abingdon, Oxfordshire OX13 6BB (GB).		
54) Title: SPRAYABLE ETHYLENE BASED HOT MI	ELT AI	DHESIVES
57) Abstract		
This invention relates to sprayable hot melt adhesive	e comp	ositions comprising an ethylene polymer and a tackifier.
·		
		<i>'</i>
·		
		•

### FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE.	
BB	Barbados	GR	Greece	NL NL	Niger
BE	Belgium	HU	Hungary	NO.	Netherlands
BF	Burkina Faso	(E	Ireland		Norway
BG	Bulgaria	IT	kaly	NZ	New Zealand
BJ	Benin	JP	Japan	PL	Poland
BR	Brazil	KE	Kenya	PT	Portugal
BY	Belarus	KG	•	RO	Romania
CA	Canada	KP	Kyrgystan	RU	Russian Federation
CF	Central African Republic	K.	Democratic People's Republic	SD	Sudan
CG	Congo	trn.	of Korea	SE	Sweden
CH	Switzerland	KR	Republic of Korea	\$G	Singapore
CI	Côte d'Ivoire	KZ	Kazakhstan	SI	Slovenia
CM	Cameroon	LI	Liechtenstein	SK	Slovakia
CN		LK	Sri Lanka	SN	Senegal
	China	LR	Liberia	SZ	Swaziland
CS	Czechosiovakia	LT	Lithuania	TD	Chad
CZ	Czech Republic	LU	Luxembourg	TG	Togo
DE	Germany	LV	Larvia	TJ	Tajikistan
DK	Denmark	MC	Monaco	TT	Trinidad and Tobago
EE	Estonia	MD	Republic of Moldova	UA	Ukraine
ES	Spain	MG	Madagascar	UG	Uganda
FI	Finland	ML	Mali	US	United States of America
FR	France	MN	Mongolia	UZ	Uzbekistan
GA	Gabon	MR	Mauritania	VN	Viet Nam

### Sprayable Ethylene Based Hot Melt Adhesives

Inventors: Michel Faissat and Herman Robberechts

#### 5 Field of the Invention

This invention relates to sprayable hot melt adhesives based upon ethylene copolymers and methods to apply these hot melt adhesives, particularly in disposable packaging and assembly applications and articles produced by such methods.

#### Background of the Invention.

- Sprayable hot melt adhesives are desirable for the economic and commercial reasons that they can be thinly, evenly and quickly coated onto a substrate, saving in both time and material, and that they allow better substrate coverage per quantity of adhesive. (Typical
- sprayable hot melt adhesives comprise an amorphous copolymer, generally a butene based copolymer of a styrene based block copolymer, combined with a tackifier.) For example, U.S. Patent 4,959,207 discloses sprayable hot melt adhesives of butene copolymers having
- up to 5.5 to 10 weight % ethylene, tackifier and amorphous diluent having a softening point greater than 90 °C. Similarly, EP 442 045 A2 discloses sprayable hot melt adhesives of amorphous polyalphaolefins having 3 to 75 weight % C4 to C10 alpha-olefin, 25 to 95 weight %
- propylene 0 to 20 weight % ethylene. In the past attempts have been made to produce sprayable ethylene  $\alpha$ -olefin copolymer based hot melt adhesives. However, these blends were unsuccessful because the polymer would coagulate at the (nozzle head) or give uneven coating
- patterns of spots of unequal size rather than a regular even coating pattern. JP- 4180981 A addresses the problem of coagulation at the nozzle head by disclosing

a hot melt adhesives of wax, bivalent phenol stabilizer, partially maleated or fumarated rosin ester tackifier and ethylene copolymer of ethylene mono-carboxylic vinyl ester/acrylic ester and suggesting that they will not clog the nozzle head when sprayed. However, when actually sprayed these hot melt adhesives will not produce a regular even pattern.

Similarly, WO 94 10256 discloses ethylene copolymer

blends for hot melt adhesives. However these blends are
not suggested for use in spraying applications.

Thus, this invention provides new sprayable hot melt adhesive compositions based upon ethylene copolymers.

Summary of the Invention.

15

This invention relates firstly to sprayable hot melt adhesive compositions comprising: a tackifier and an ethylene polymer having up to 40 weight % comonomer, based upon the weight of the copolymer; a CDBI of 50% or greater; a melt index of 5 or more; and an Mw/Mn of 6 or less and secondly, to a process for spraying ethylene homopolymers and copolymers comprising selecting a hot melt adhesive composition as described above and atomizing, spiral spraying or melt blowing the hot melt adhesive selected onto a substrate.

## Detailed Description

In a preferred embodiment, this invention relates to sprayable hot melt adhesive compositions comprising: a tackifier, and an ethylene polymer having up to 30 weight % of a comonomer, based upon the weight of the copolymer; a CDBI of 60% or greater; a melt index of 5 or more; and an Mw/Mn of 6 or less.

Preferred ethylene polymers that can be used in the practice of this invention include ethylene homopolymers and copolymers. The copolymers preferably have up to 40 weight %, preferably up to 30 weight %, even more preferably from 5 to 30 weight %, even more preferably from about 10 to about 25 weight %, based upon the weight of the copolymer, of one or more comonomers. Preferred comonomers may be a  $C_3$  to  $C_{40}$  linear, branched or cyclic alpha-olefin. In a preferred embodiment the comonomer is a  $C_3$  to  $C_{20}$  alpha olefin, and in a 10 particularly preferred embodiment the comonomer is butene-1, pentene-1, hexene-1, heptene-1, octene-1, nonene-1, decene-1, undecene-1, dodecene-1, 3,5,5trimethyl hexene-1, 3-methylpentene-1, 4-methylpentene-1 and the like. Terpolymers of ethylene with two or more of the above monomers are also useful in the practice of this invention.

In another preferred embodiment the ethylene polymers

20 used in this invention have a Composition Distribution
Breadth Index (CDBI) of 50% or more, preferably of 60%

or more, even more preferably of 70% or more, even

more preferably of 80% or more. CDBI is a measure of
the uniformity of comonomer distribution within a given

25 sample and is measured according to the method described
in PCT publication WO 93-03093, published February 18,
1993. A homopolymer has a CDBI of 100%.

In another preferred embodiment the ethylene polymers
used in this invention have an Mw/Mn of 6 or less, more
preferably 5 or less, even more preferably 4 or less,
even more preferably 3 or less, even more between 2 and
1.

In another preferred embodiment the ethylene polymers used in this invention have a melt index as measured by ASTM 1238, condition E, of 5 dg/min or more, preferably

15 dg/min or more, even more preferably 30 dg/min or more, even more preferably between about 100 and 10,000 dg/min.

In another preferred embodiment, the ethylene polymers of this invention are at least 50 % amorphous, preferably between 60 and 100% amorphous, even more preferably between 70 and 100% amorphous. Percent amorphous content is determined by Differential Scanning Calorimetry measurement according to ASTM E 794-85.

Preferred tackifier that may be blended with the ethylene copolymers described above are those typically used in the art. Examples include, but are not limited to, aliphatic hydrocarbon resins, aromatic modified aliphatic hydrocarbon resins, hydrogenated polycyclopentadiene resins, polycyclopentadiene resins, gum rosins, gum rosin esters, wood rosins, wood rosin esters, tall oil rosins, tall oil rosin esters,

- polyterpenes, aromatic modified polyterpenes, terpene phenolics, aromatic modified hydrogenated polycyclopentadiene resins, hydrogenated aliphatic resin, hydrogenated aliphatic aromatic resins, hydrogenated terpenes and modified terpenes, and
- hydrogenated rosin esters. In a preferred embodiment the tackifier is hydrogenated. In another preferred embodiment the tackifier is non-polar. (Non-polar meaning that the tackifier is substantially free of monomers having polar groups. Preferably the polar
- groups are not present, however if they are preferably they are not present at more that 5 weight %, preferably not more that 2 weith %, even more preferably no more than 0.5 weight %.) In a preferred embodiment the tackifier has a softening point (Ring and Ball, as
- measured by ASTM E-28) of 80 °C to 140 °C, preferably 100 °C to 130 °C.

WO 97/15636 PCT/EP96/03855

-5-

The tackifier is typically present at about 15 weight % to about 75 weight %, based upon the weight of the blend, more preferably 30 weight % to 65 weight %, even more preferably 40 weight % to 60 weight %. In a preferred embodiment the tackifier can be a blend of two or more tackifiers. In another preferred embodiment the tackifier comprises a blend of two or more hydrogenated polycyclopentadiene resin. The 5000 series of ESCOREZTM resins are preferred tackifiers.

10

25

30

35

The ethylene polymer and the tackifier may be blended together by methods known in the art. For example the ethylene copolymer and the tackifiers can be physically admixed, they can be melt blended, they can be master batched, they can be solvent blended and the like. one non-limiting example, the polymer and the tackifier are melted in a Z-blade mixer of in a Brabender twin screw extruder and blended under high shear conditions. Their blend components should be chosen so that a final blend viscosity of 20,000 mPaS or less is obtained, preferably 15,000 or less, even more preferably 10,000 or less, even more preferably 8,000 or less even more preferably between 500 and 8000. The range of 500 to 5000 mPa.s at 180°C is ideal for spraying a low coating weight and wide spray pattern (spiral, net like web, or nebulized droplets).

In addition to the polymer and the tackifier, one can add another polymer ("second polymer"). Preferred polymers include any of the polymers described above as ethylene polymers and polymers of ethylene and a polar monomer. The polar monomer is preferablu present at up to about 45 weight %, even more preferably up to about 0.5 to about 33 weight %. Preferred polar comonomers may be an ester, a carboxylic acid, an acrylic, and acrylic ester, a vinyl ester or the like. In a preferred embodiment the polar monomer is a vinyl ester

or an alkyl acrylic ester, such as vinyl acetate, acrylic acid, methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, methacrylic acid, ethacrylic acid, and derivatives thereof.

5

The second polymer may be present at up to 50 weight %, preferably 0.1 weight % to 30 weight %. A preferred class of polymer to be added to the composition is an ethylene/propylene/butene terpolymer.

Ethylene/propylene/ butene terpolymers are not typically 10 sprayable, however, when blended with the ethylene polymers described above, they can be formed into sprayable compositions. Examples of preferred ethylene/propylene/butene terpolymers are VESTOPLAST™

708, VESTOPLASTM750, and VESTOPLASTM408 which are 15 commercially available from Hüls. The ethylene/propylene/butene terpolymer is preferably present at up to 50 weight %, even more preferably at 0.1 weight % to 20 weight %, even more preferably at 0.1 20

weight % to 15 weight %.

Another optional component of the ethylene polymer/tackifier composition is a(plasticizer) Preferred plasticizers include(mineral oils)

- polybutenes, phthalates and the like. Particularly preferred plasticizers include phthalates such as diisoundecyl phthalate (DIUP), diisononylphthalate (DINP), dioctylphthalates (DOP) and the like. Another optional component of the ethylene
- polymer/tackifier composition is a low molecular weight 30 product such as wax, oil or low Mn polymer, (low meaning below Mn of 5000, preferably below 4000, more preferably below 3000, even more preferably below 2500). oils include aliphatic napthenic oils. Preferred low Mn
- polymers include polymers of lower alpha olefins such as 35 propylene, butene, pentene, hexene and the like. A particularly preferred polymer includes polybutene

15

having an Mn of less than 1000. An example of such a polymer is available under the trade name PARAPOL™ 950 from Exxon Chemical Company. PARAPOL™ 950 is an liquid polybutene polymer having an Mn of 950 and a kinematic viscosity of 220cSt at 100 °C, as measured by ASTM D 445.

The blend may then be applied directly to a substrate as a hot melt adhesive or may be sprayed thereon. (Spraying is defined to include atomizing, spiral spray controlled fiberization and melt blown techniques.) Melt blown techniques are defined to include the methods described in U.S. patent 5,145,689 or any process where air streams are used to break up filaments of the extrudate and then used to deposit the broken filaments on a substrate. In general, melt blown techniques are processes that use air to spin hot melt adhesive fibers and convey them onto a substrate for bonding. Fibers sizes can easily be controlled from 20-200 microns by changing the melt to air ratio. Few, preferably no, stray fibers are generated due to the inherent stability of adhesive melt blown applicators. Under UV light the bonding appears as a regular, smooth, stretched dots pattern. Atomization is a process that uses air to atomize hot melt adhesive into very small dots and convey them onto a substrate for bonding.

The blend may also be applied to a substrate using conventional techniques for applying a hot melt adhesive to a substrate. Examples include hot melt jet nozzle coating, hot melt multiline coating, hot melt slot die coating, hot melt wheel coating, hot melt roller coating, and solvent roller coating.

In a preferred embodiment the blend is applied to a substrate using a spiral spray. Spiral spray is a method used for producing a filamentary spiral application. In one example the hot melt adhesive and

spray air are mixed inside the nozzle, eliminating external influences on the spray pattern. In another example, the hot melt adhesive is drawn into a small fiber by high-velocity air jets. The fiber is then rotated by jets until it contacts the substrate, producing a helical pattern from the single strand of adhesive.

The sprayed hot melt adhesives of this invention can be

10 used for disposible diaper and napkin chasis
construction, elastic attachment in disposable goods
converting, packaging, labelling and other assembly
applications. Particularly preferred applications
include: baby diaper leg elastic, diaper frontal tape,

15 diaper standing leg cuff, diaper chassis construction,
diaper core stabilization, diaper liquid transfer layer,
diaper outer cover lamination, diaper elastic cuff
lamination, feminine napkin core stabilization, feminine
napking adhesive strip, industrial filtration bonding,

20 industrial filter material lamination, filter mask
lamination, surgical gown lamination, surgical drape

Tests and Materials.

25

CDBI was measured according to the procedure described in PCT publication WO 93-03093, published February 18, 1993.

Melt Index (MI) was measured according to ASTM 1238, condition E (dg/min).

lamination, and perishable products packaging.

Density was measured according to ASTM D-792 (g/cc).
T-Peel was measured ASTM D1876-72 (20 mm wide test specimens and 2 inch/min (5.08 cm/ min) head speed)
Viscosity was measured according to ASTM D 3236 at 180 °C (mPaS)

Penetration was measured according to ASTM D1321-86.

SAFT (Shear Adhesion Fail Temperature) was measured by adhereing a coated polyethylene strip of 25 mm width to stainless steel via press lamination with a contact area of 12.5mm x 25mm, hanging samples in an oven held at 25  $^{\circ}$ 

- C and suspending a 500 gram weight from the bottom of the strip. The temperature is raised at 0.4 °C/min and the bond failure temperature is measured. The SAFT is the average of three test samples. (°C).
- Hot Shear was measured by suspending a 1000 gram weight from a 25 mm wide strip of polyethylene film coated with the adhesive formulation which is adhered with press lamination to a stainless steel plate with a contact area of 12.5mm x 25mm. The sample is placed in a ventilated oven at 40 °C. Every 30 minutes the
- temperature is increased by 10°C. Time and temperature are recorded until stress failure occurs. Typically these tests are made and recorded individually to determine the reliability of the holding power. (min, °C)
- Sprayability was measured on a CT 325 Meltex coater under the conditions listed in Example 1. Perfect spiral is shown in figure 1, acceptable spiral is shown in figure 2 and no spiral but unequal spots is shown in figure 3.
- 25 Static shear was measured according to hot shear test set-up described above, but temperature is maintained constant at 50 °C. Time is recorded until stress failure occurs.
- Molecular weights (Mw and Mn) were measured by Gel

  Permeation Chromotography, unless otherwise noted, using
  a Waters 150-CV Gel Permeation Chromatograph equipped
  with a differential refractive index (DRI) detector and
  polystyrene standards. Polymer samples were dissolved
  in trichlorobenzene solvent at 165 °C and the solutions
- were run at 145 °C using three Shodex GPC AT-80 M/S columns in series. This general technique is discussed in "Liquid Chromotography of Polymers and Related

Materials III'" J. Cazes Ed., Marcel Decker, 1981, page 207, which is incorporated by reference herein. corrections for column spreading were employed; however, data on generally accepted standards, e.g. National

- Bureau of Standards Polyethylene 1475, demonstrated a precision with 0.1 units for Mw/Mn which was calculated from elution times. The numerical analyses were performed using Expert  $\mathsf{Ease}^\mathsf{TM}$  software available from Waters Corporation.
- Melt Flow Rate (MFR) was measured according to ASTM\_D 1238 (10 kg, 230 °C)

EXACTTM 4038 is an ethylene butene copolymer having an MI of 125 dg/min, a density of 0.885 g/cc, a butene content

- of 19 weight percent based upon the weight of the copolymer, an Mw/Mn of 2.06 and a CDBI over 50%, and a crystallinity of about 16%.
  - EXACTTM 4044 is an ethylene hexene copolymer having an MI of 16.5 dg/min, a density of 0.895 g/cc, a hexene
- content of 20 weight %, an Mw/Mn of 1.97 and a CDBI over 20 50 %, and a crystallinity of about 24%.
  - EXACT™ 4023 is an ethylene butene copolymer having an MI of 35 dg/min, a density of 0.882 g/cc, a butene content of 21 weight %, an Mw/Mn of 2.21 and a CDBI over 50%,
- and a crystallinity of about 13%. 25 PARAPO1™ 950 is a liquid polybutene having an Mn of about 950 and a Kinematic viscosity of 220 cst at 100 °c, as measured by ASTM D445.
- ESCOREZ™ 5380 is a hydrogenated polycyclopentadiene tackifier having a softening point of 85 °C. ESCOREZ™ 5320 is a hydrogenated polycyclopentadiene tackifier having a softening point of 125 °C. ESCORENE™ UL 40028 is an ethylene/vinyl actetate copolymer having an MI of 400 dg/min, and a VA content
- 35 of 28%.

-11-

VESTOPLAST<sup>M750</sup> is an ethylene/propylene/butene copolymer available from Huls, having a density of 0.87 and an MV of 70,000.

VESTOPLAST ™708 is an ethylene/propylene/butene copolymer available from Huls, having a density of 0.87 and an MV of 45,000.

DIUP is diisoundecyl pthalate

Meltex CT 325 is a coating machine from Nordson/Meltex. EP 34-6SD spray head is a spiral spray coating head.

IRGANOXTM 1010 is an antioxidant available form Ciba Geigy described in U.S. Patents 3,285,855 and 3,644,482.

#### Examples

Several diffferent ethylene copolymers were blended with one or more tackifiers according to the following procedure. In a Z-blade mixer with the rotorblades in Z-shape, 204 grams of the ethylene copolymer and 276 grams of tackifying resin were blended incrementally at 180 °C, under nitrogen, until the total volume of the polymer and tackifier were mixed. The components were

allowed to mix for 10 minutes, then the parapol DIUP, etc, if any, were added. The blend was then mixed for another 50 minutes and poured into a release paper container. Several tests were performed on the various

blends according to the procedures described above and the blends were sprayed using a CT 325 Meltex coater under the following conditions:

Melt section temp.: 170°c

Hoze temp.: 175°c

Nozzle temp.: 175°c 30

Air temp.: 200°c

12 notches spiralhead

Nip roll: 1 bar

Brake roll 1: 0-0.5 bar

Brake roll 2: 0-0.5 bar

Unwind 1: 0-0.5 bar

Lamination roll 1: 4 bar

Lamination roll 2: 4 bar

Umwind 2: 0-0.5 bar

Cooling Unit: 15-16°C

Webspeed: 125 m/min

pumpspeed between 40-50 rpm on TACHO to have a coating weight of  $\pm$  0.5 g/lm for a spiral diameter of 4-4.5 cm

The polymers, blend components and data are reported in Tables 1 to 4.

- 10 Symbols in the Tables
  1 = g/spiral spray ±4cm, Adhesive spiral sprayed onto a nonwoven coverstock of thermally bonded polypropylene and then bonded to a polyethylene substrate.
- 2 = Adhesive coated onto polyethylene substrate then
  bonded to another polyethylene substrate.
  3= adhesive meltblown onto a nonwoven coverstock of thermally bonded polypropylene then bonded to polyethylene substrate.
- Perfect blownability means that the adhesive was deposited evenly with the same coating weight left to right on the substrate.

AF = adhesive failure, CF = cohesive failure. Perfect blownability means that the adhesive was deposited evenly with the same coating weight left to right on the substrate.

Perfect spiral means that the spiral is a wide and regular spiral of about 4 cm.

TABLE 1

	Blend A	Blend B	Blend C	Blend D
Exact 4038	50	40	34	-
Exact 4044	-	-	-	40
Escorez 5380	38	43	46	40
Parapol 950	12	17	20	20
Irganox 1010	0.5	0.5	0.5	0.5
Sprayability	acceptable	good	perfect	no spiral
4-4.5 cm	spiral	spiral	spiral	but
spiral width				unequal
				spots
Sprayability	perfect	perfect	perfect	no spiral
2-2.5 cm	spiral	spiral	spiral	but
spiral width		İ	1	unequal
T Dool NEG (DD			ļ	spots
T-Peel NWC/PE @ R.T. <sup>1</sup>	l '	475	540	-
	g/spray	g/spray		
Failure mode		adhesive		
T-Peel NWC/PE	· · · · · · · · · · · · · · · · · · ·	60	50	
@ 40 °C <sup>1</sup>	g/spray	g/spray	g/spray	
Failure mode	adhesive	adhesive	adhesive	
blend	13700	6900	3650	22750
viscosity @	1			
180 °C (mpas)				
Hot shear			11,50	
(min,°C)			11,50	
			13,50	ļ
Static shear			11	
@ 50 °C (min)				
SAFT (°C)			53/53/51	
Penetration @			3.12	
RT (mm)				ĺ
Penetration @			6.72	
40 °C	]	ł	_	
T-Peel PE/PE			1285	
<pre>@ R.T.2(g/cm)</pre>			1200	
Failure mode		•	cohesive	
T-Peel PE/PE			315	
@ 40°C <sup>2</sup> (g/cm)				
Failure mode			cohesive	

TABLE 2

		- ADDE 2	
Exact 4038	Blend I		F Blend G
Vestoplast 750	20	15	-
Vestoplast 708			15
Escorene UL		35	35
40028	30	-	-
Escorez 5380	38	38	38
Parapol 950	12	12	12
Irganox 1010	0.5	0.5	0.5
Sprayability	acceptable	eacceptabl	e no spiral
4-4.5 cm spiral	spiral	spiral	but
width			unequal
			spots
Sprayability	perfect	perfect	no spiral/
2-2.5 cm spiral	spiral	spiral	unequal
width		-	spots
T-Peel NWC/PE	655	480	, , , , ,
@ R.T.1	g/spray	g/spray	
Failure mode	adhesive		
T-Peel NWC/PE	120	160	<del></del>
@ 40 °C1	g/spray	g/spray	
Failure mode	adhesive	adhesive	<del></del>
blend viscosity	8400	3920	3000
@ 180 °C (mpas)			3000
Hot shear			12,50
(min,°C)			12,50
			13.50
Static shear			13.30
9 50 °C(min)			13
SAFT(°C)			60/60/60
Penetration (mm)		<del></del>	
@ R.T.	1	Ĭ	2.02
Penetration (mm)			4 50
º 40°C			4.72
T-Peel PE/PEZ			- 500 3 -
(g/cm)@ R.T.			590 AF
11			1177.000.
Blownability	1		
slownability	1	-	unaccept-
G-Peel PE/PE2			able 385 AF

TABLE 3

	Blend H	Blend I	Blend J
Exact 4023			24
Exact 4038	34		
Exact 4044		24	
Escorez 5380	23	28	28
Escorez 5320	23	28	28
Parapol 950	20	20	20
Irganox 1010	0.5	0.5	0.5
Sprayability 4-4.5 cm	perfect	not good	perfect
spiral width	spiral		spiral
Sprayability 2-2.5 cm	perfect	perfect	perfect
spiral width	spiral	for 1 cm	spiral
T-Peel NWC/PE	875	120	610
@ R.T. <sup>1</sup>	g/spray	g/spray	g/spray
Failure mode	adhesive	adhesive	adhesive
T-Peel NWC/PE	340	350	400
@ 40 °C <sup>1</sup>	g/spray	g/spray	g/spray
Failure mode	adhesive	adhesive	adhesive
blend viscosity	4500	11720	5660
@ 180 °C (mpas)			
Hot shear	7,60	16,70	5,60
(min, °C)	7,60	18,70	5,60
	5,60		5,60
Static shear	25	298	21
<pre></pre>			
SAFT (°C)	60/60/60	72/72/71	60/59/59
Penetration (mm)	2.73	0.90	2.06
@ R.T.			
Penetration (mm)	5.79	2.75	7.14
⊇ 40 °C			
T-PEEL PE/PE <sup>2</sup> (g/cm)@ R.T.	1340 CF	2145 CF	1515 CF
T-PEEL PE/PE <sup>2</sup> (g/cm)@ 40°C	425 CF	1100 AF/CF	865 CF
Blownability	perfect		perfect
T-PEEL NWC/PE3	2.35 AF		3.50 T
"Melt Blown" (N/25mm)@ R.T.			
T-PEEL NWC/PE3	0.65 AF		2.15 AF
"Melt Blown" (N/25mm)@ 40°C			

TABLE 4

	<del></del>
	Blend L
25	34
55	46
20	20
0.5	0.5
perfect	perfect
spiral	spiral
perfect	perfect
spiral	spiral
600	650
g/spray	g/spray
adhesive	adhesive
350	280
	g/spray
adhesive	adhesive
2800	5680
13,60	16,60
11,60	13,60
7,60	16,60
>3000	117
66/65/63	62/64/63
1.10	1.70
5.07	5.38
1425 CF	1350 CF
715 CF	660 CF
perfect	perfect
0.70 AF	1.80 AF
1.25 AF	0.95 AF
	55 20 0.5 perfect spiral perfect spiral 600 g/spray adhesive 350  adhesive 2800  13,60 11,60 7,60 >3000 66/65/63 1.10 5.07 1425 CF 715 CF perfect 0.70 AF

All documents described herein are incorporated by reference herein, including any priority documents and/or testing procedures. As is apparent from the 5 foregoing general description and the specific embodiments, while forms of the invention have been illustrated and described, various modifications can be made without departing from the spirit and scope of the invention. Accordingly, it is not intended that the invention be limited thereby.

#### Claims:

- A process for spraying ethylene homopolymers and copolymers comprising selecting a hot melt adhesive composition comprising: a tackifier and an ethylene polymer having up to 40 weight % comonomer, based upon the weight of the copolymer; a CDBI of 50% or greater; an MI of 5 or more; and an Mw/Mn of 6 or less, and atomizing, spiral spraying or melt blowing the hot melt adhesive selected onto a substrate.
- The process of claim 1 wherein the comonomer is a C<sub>2</sub> to C<sub>40</sub> linear, cyclic or branched alpha-olefin, preferably butene, hexene and/or octene, preferably present at up to about 40 weight %.
  - 3. The process of any of the above claims further comprising a second polymer.
  - 4. The process of claim 3 wherein the second polymer is an ethylene/propylene/butene terpolymer.
- 5. The process of claim 3 or 4 wherein the second polymer is present at up to 50 weight percent based upon the weight of the first and second polymers.
  - 6. The process of any of the above claims wherein plasticizer is additionally present.
  - 7. The process of claim 6 wherein the plasticizer is a pthalate, preferably diisoundecyl pthalate.
- 8. The process of any of the above claims wherein an oil or wax is additionally present, preferably the oil is an olefinic or napthenic oil.

20

- 9. The process of any of the above claims wherein a polybutene copolymer having an Mn of less than 2500 is additionally present.
- 5 10. The process of any of the above claims where the tackifier is aliphatic hydrocarbon resins, aromatic modified aliphatic hydrocarbon resins, hydrogenated polycyclopentadiene resins, polycyclopentadiene resins, gum rosins, gum rosin esters, wood rosins, wood rosin
- esters, tall oil rosins, tall oil rosin esters, polyterpenes, aromatic modified polyterpenes, terpene phenolics, aromatic modified hydrogenated polycyclopentediene resins, hydrogenated aliphatic resin, hydrogenated aliphatic aromatic resins,
- 15 hydrogentated terpenes and modified terpenes, and hydrogenated rosin esters.
  - 11. The process of any of the above claims wherein the tackifier is a hydrogenated, linear, cyclic and/or branched pentadiene.
  - 12. The process of any of the above claims wherein the tackifier comprises hydrogenated polycyclopentadiene resin.

25

20

- 13. The process of any of the above claims wherein the tackifier comprises a blend of two or more hydrogenated polycyclopentadiene resin.
- 30 14. A process for spraying ethylene/propylene/butene terpolymers comprising:

selecting a hot melt adhesive composition comprising

a ethylene copolymer having up to 40 weight %

comonomer, based upon the weight of the polymer; a CDBI

of 50% or greater; an MI of 5 dg/min or more; and an

-19-

Mw/Mn of 6 or less with a tackifier, an optional plasticizer, an optional antioxidant and the terpolymer.

#### INTERNATIONAL SEARCH REPORT

Inte: onal Application No PC I/EP 96/03855

		Į PL	CI/EP 96/03855
A. CLASS IPC 6	IFICATION OF SUBJECT MATTER C09J123/16		
According	to International Patent Classification (IPC) or to both national c	assification and IPC	
	S SEARCHED	and the	
	documentation searched (dassification system followed by dassi CO9J	lication symbols)	
Documenta	tion searched other than minimum documentation to the extent (	hat such documents are included	in the fields searched
Electronic	iata base consulted during the international search (name of data	base and, where practical, search	h (erms used)
C. DOCUM	MENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of ti	ne relevant passages	Relevant to claim No.
Y	WO,A,92 12212 (EXXON CHEMICAL F 23 July 1992	·	1,2,8-14
	see page 4, line 6 - page 5, li see page 9, line 37 - page 10,		
Y	WO,A,94 10256 (EXXON CHEMICAL F 11 May 1994 cited in the application	PATENTS INC)	1-5,8-14
	see page 3, line 42 - line 58		
Y	EP,A,O 442 045 (HUELS CHEMISCHE 21 August 1991 cited in the application see page 7, line 1 - page 9, li	·	3-5
		-/	
		-,	
LA) End	her documents are listed in the continuation of box C.	V Patent (amily memb	ers are listed in annex.
<u> </u>		X Patent family memb	G. Et ibid iii buak
"A" docum	tegories of cited documents :  ent defining the general state of the art which is not  ered to be of particular relevance.	or priority date and not cited to understand the	i after the international filing date in conflict with the application but principle or theory underlying the
"E" earlier filing o	document but published on or after the international	cannot be considered no	relevance; the claimed invention ovel or cannot be considered to o when the document is taken alone
which author	is cated to establish the publication date of another in or other special reason (as specified) ent referring to an oral disclosure, use, exhibition or	'Y' document of particular r cannot be considered to	o when the document is usen alone relevance; the claimed invention involve an inventive step when the with one or more other such docu-
	means ent published prior to the international filing date but tain the priority date claimed	ments, such combination in the art. '&' document member of the	n being obvious to a person skilled r same patent family
	actual completion of the international search	Date of mailing of the in	•
	6 December 1996	2 2. 01	i. J <i>i</i>
.vens ere f	European Patent Office, P.B. 5818 Patentiaan 2 NL - 2220 HV Rupwitk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,	Schmidt, H	
	Fax (+31-70) 340-3016	Scinarut, n	

Form PCT-ISA-210 (second sheet) (July 1992)

. 1

## INTERNATIONAL SEARCH REPORT

Inter nal Application No PCI/EP 96/03855

C1(Connum	IDON) DOCUMENTS CONSIDERED TO BE RELEVANT	C1/EP 90/03855	
Category *		Relevant to claim No.	
A	W0,A,92 05217 (PLAN B INC) 2 April 1992 see page 5, line 27 - page 6, line 12 see page 9, line 18 - line 35 see page 12, line 1 - page 13, line 32 see page 17, line 26 - line 28	1-14	
٠			
	·		

1

#### INTERNATIONAL SEARCH REPORT

Intermal Application No PC I / EP 96/03855

Patent document cated in search report	Publication date	Patent family member(s)		Publication date
WO-A-9212212		CA-A-	2097303	28-06-92
		DE-D-	69117534	04-04-96
		DE-T-	69117534	14-08-96
		EP-A-	0564596	13-10-93
		ES-T-	2084346	01-05-96
		JP-T-	6504082	12-05-94
WO-A-9410256	11-05-94	CA-A-	2148353	11-05-94
		EP-A-	0666890	16-08-95
		JP-T-	8503722	23-04-96
		US-A-	5548014	20-08-96
EP-A-0442045	21-08-91	DE-A-	4000696	18-07-91
		DE-D-	59003015	11-11-93
		ES-T-	2044375	01-01-94
UO A 0205217	02 04 02			
WO-A-9205217	02-04-92	AU-A-	8627691	15-04-92
		US-A-	5404692	11-04-95